# Low Temperature Studies (12—293 K) of Unstable Species using Nujol Mulls: Reversible Carbon Monoxide Ejection and Carbon–Hydrogen Bond Activation

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Infrared spectroscopic experiments using $[W(CO)_6]$ and $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$, which have previously been studied in gas matrices by matrix isolation spectroscopy, are presented which demonstrate that Nujol mulls can function as *pseudo* matrices over the temperature range 12—293 K, thereby considerably enhancing the usefulness and availability of low temperature studies of unstable species, especially for those derived from involatile precursors.

The matrix isolation technique[1] has proved to be extremely useful for trapping and characterising unstable species related to reaction intermediates proposed on the basis of kinetic measurements. This has been particularly true for unstable organometallic species proposed in reaction schemes and catalytic cycles.[2] The success of the technique in this field has arisen because many organometallic and also organic compounds are volatile and can be condensed along with high purity matrix gases, *e.g.* Ar, Kr, Xe (99.999%). There are, however, many compounds which are involatile, *e.g.* inorganic co-ordination complexes, or decompose on attempted volatilisation, *e.g.* phosphine complexes. Unstable species derived from such parent compounds cannot be studied by the gas matrix technique. As part of a survey of alternative matrix media, *e.g.* solvent cast polymer films [poly(vinyl chloride),[3,4] poly(vinyl alcohol)[5]], paraffin wax,[3] and alkali halide discs,[6] we report here some low temperature studies (12—293 K) of species in Nujol mulls.

Irradiation of a Nujol mull containing $[W(CO)_6]$ [2 mg in 2 drops (*ca.* 40 mg)] at 77 K,† using a filtered medium pressure Hg arc ($\lambda < 350$ nm, 15 min), gave new i.r. bands at 2089w, 1953s, and 1925m $cm^{-1}$, which can be assigned to $[W(CO)_5]$ by comparison with data for other media,‡ together with a band at 2132 $cm^{-1}$ which corresponds to free CO [Figure 1 (a)—(c)]. On warming the mull to *ca.* 150 K reversal of the primary photoprocess rapidly occurred [Figure 1(d)].

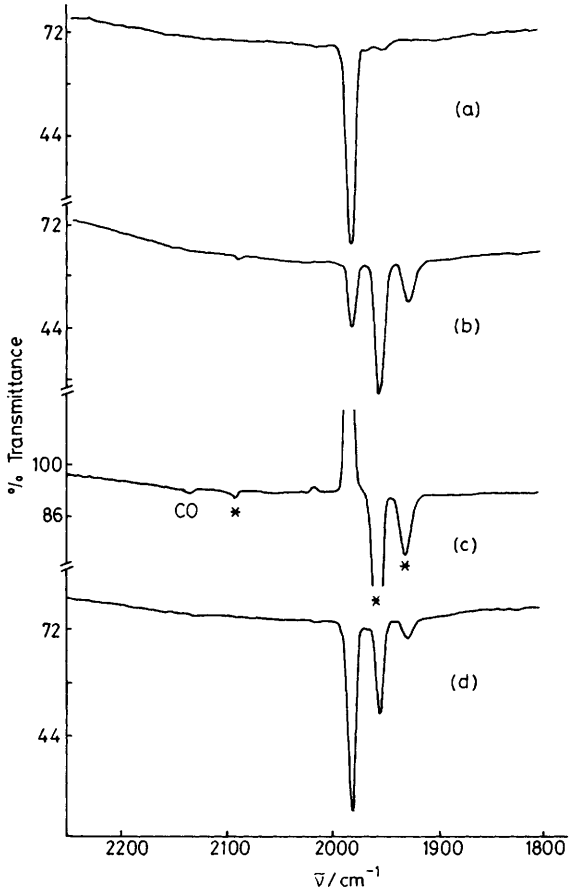


**Figure 1.** I.r. spectra from an experiment with $[W(CO)_6]$ in a Nujol mull: (a) before photolysis (77 K); (b) after photolysis ($\lambda$ <350 and >550 nm, 15 min) at 77 K; (c) ratio spectrum (b)/(a); and (d) after warming to *ca.* 150 K. Bands marked with an asterisk (*) arise from $[W(CO)_5]$.

† All Nujol mulls and KBr discs were mounted between $CaF_2$ (Nujol mulls) or CsI (KBr discs) windows and cooled to 77 K [liquid $N_2$; glass cryostat,[3,7] (Applied Photophysics model No 700)] or 12 K [closed-cycle liquid He cryostat (Air Products and Chemicals CSA/W 202 Displex)] at $10^{-3}$ and $10^{-6}$ Torr, respectively. I.r. spectra were recorded using a Nicolet 7199 Fourier transform i.r. spectrometer (1 $cm^{-1}$ resolution; number of data points 16 384, number of transient points 32 768, number of scans 200). Filters for wavelength photolysis are described elsewhere.[3,8]

‡ $\nu_{CO}$ at: $CH_4$ (2092w, 1957s, 1926m $cm^{-1}$),[9] poly(vinyl chloride) (2084w, 1946s, 1918sh $cm^{-1}$),[3] paraffin wax (2090w, 1956s, 1929m $cm^{-1}$).[3]

**Table 1.** Observed terminal CO stretching band positions ($cm^{-1}$) for $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$ and its photoproducts in various low temperature media at 12 and 77 K.

| | | | Low temperature medium (temperature) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Ar matrix[a] | $CH_4$ matrix[a] | Nujol mull[b] | | Wax disc[b] | Perfluorokerosine mull[b] | | KBr disc[b] |
| Compound | (12 K) | (12 K) | (12 K) | (77 K) | (77 K) | (12 K) | (77 K) | (12 K) |
| $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$ | 2025s | 2021s | 2016s | 2016s | 2018s | 1998s | 1999s | 1998s |
| | 1959s | 1954s | 1948s | 1948s | 1928s | 1928s | 1928s | 1927s |
| $[(\eta^5\text{-}C_5Me_5)Ir(CO)]$ | – | – | 1958 | 1959 | 1968 | – | – | 1939 |
| $[(\eta^5\text{-}C_5Me_5)Ir(CO)(H)(R)]$ | – | 1991[c] | – | 1978[d,e] | 1983[d,e] | – | – | – |
| CO | – | 2137 | 2130 | 2132 | 2132 | 2134 | – | 2134 |

[a] Data from ref. 8. [b] This work. [c] R = Me. [d] R = $-(CH_2)_nMe$, see text. [e] Band intensity increasing with increasing temperature.

It has recently been shown that photolysis of $[(\eta^5\text{-}C_5R_5)M(CO)_2]$ (R = H, Me; M = Rh, Ir) complexes in $CH_4$ matrices at *ca.* 12 K produces hydrido methyl complexes, $[(\eta^5\text{-}C_5R_5)M(CO)(H)Me]$, which arise from cleavage of C–H bonds in $CH_4$, *i.e.* photoactivation of $CH_4$ has occurred. Irradiation ($\lambda < 280$ and $> 550$ nm) of $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$ in Nujol mulls at 77 K produced free CO (2130 $cm^{-1}$) and two new bands located between those of the parent dicarbonyl complex were observed. On raising the temperature the intensity of the new band at 1978 $cm^{-1}$ increased while that of the 1958 $cm^{-1}$ band decreased; only the 1958 $cm^{-1}$ band was observed at 12 K. On the basis of previous work with $[(\eta^5\text{-}C_5R_5)M(CO)_2]$ complexes[8] and $[(\eta^5\text{-}C_5H_5)Ir(CO)(H)_2]$[10] the band at 1958 $cm^{-1}$ can be assigned to $[(\eta^5\text{-}C_5Me_5)Ir(CO)]$ while the band at 1978 $cm^{-1}$ can be assigned to $[(\eta^5\text{-}C_5Me_5)Ir(CO)(H)R']$ (Table 1), where R′ corresponds to $-(CH_2)_nMe$ in some form, arising from photoactivation of C–H bonds in Nujol. Similar behaviour was observed for wax discs at 77 K (Table 1). In an attempt to model an unreactive gas matrix, *e.g.* Ar, $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$ was photolysed in perfluorokerosine mulls and KBr discs. In the former the only detectable photoproduct was CO but in the latter a very weak band was observed at 1939 $cm^{-1}$ which may possibly be assigned to the co-ordinatively unsaturated monocarbonyl species, $[(\eta^5\text{-}C_5Me_5)Ir(CO)]$ (Table 1).

The above results illustrate that Nujol mulls, one of the simplest and commonest forms of i.r. sampling techniques, can be used to study unstable species over a wide temperature range (12—293 K). Such mulls can provide the basis for considerably less expensive and more general low temperature experiments than experiments using gas matrices. In particular, reactive species, *cf.* intermediates proposed in reaction mechanisms, can be studied which arise from compounds which are involatile and/or decompose. An important feature of studies using mulls, and also polymer films, wax discs, and alkali halide discs, is that the thermal reactions of photogenerated fragments can be monitored as the temperature rises and the final products at ambient temperatures can be related to the photoproducts formed in solution photochemical reactions. A disadvantage of mulls compared to gas matrices is that the bands are broader§ but, with the advent of Fourier transform i.r. spectrometers as routine instruments, this need not be an insurmountable problem.

Future work will aim to investigate the photophysical processes of species in Nujol and thereby to understand to what extent reactive centres are truly isolated.¶ In addition the mull technique will be applied to a variety of systems which have hitherto proved inaccessible to gas matrix isolation studies, *e.g.* metal–phosphine complexes (homogeneous catalysis using phosphine-modified catalysts).

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§ Half-widths at half-heights (absorbance) for various species in different media were as follows. $[W(CO)_6]$: $CH_4$(<1 $cm^{-1}$); Nujol (10 $cm^{-1}$); poly(vinyl chloride) (30 $cm^{-1}$); paraffin wax (15 $cm^{-1}$); $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$: $CH_4$ (<1 $cm^{-1}$); Nujol (8 $cm^{-1}$); paraffin wax (10 $cm^{-1}$); perfluorokerosine (20 $cm^{-1}$); KBr (*ca.* 50 $cm^{-1}$).

¶ In a concentration dependence study of the photophysical processes of $[Ru(bipyridyl)_3]^{2+}$ in poly(vinyl alcohol) films (250 mg) at 77 K constant lifetimes were observed over the range 0.001 to 1 mg of substrate, and even up to 10 mg the decay curves were single exponentials, *i.e.* no self-quenching occurs.[11]